PRINTED ELECTRODE FOR LIVING BODY

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Abstract

A printed electrode for a living body which is obtained by printing or directly sintering ink paste or binder on a substrate. The paste or binder contains hydrophilic fine particles consisting hydrophilic polymer or a water-soluble material, and electrically conductive fine particles. The surface area of the electrode for a living body is enlarged to a maximum to limit its deterioration and stably keep a current for a long time.

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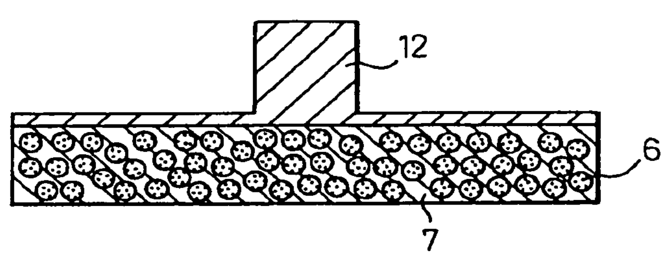
(54) PRINTED ELECTRODE FOR LIVING BODY

(57) A printed electrode for a living body which is obtained by printing or directly sintering ink paste or binder on a substrate. The paste or binder contains hydrophilic fine particles consisting hydrophilic polymer or a water-soluble material, and electrically conductive fine particles. The surface area of the electrode for a living body is enlarged to a maximum to limit its deterioration and stably keep a current for a long time.

Fig.2(a)



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Description

TECHNICAL FIELD

The present invention relates to a printed electrode for biological use such as a bioelectrode, typically, for example, an electrode for iontophoresis, an electrode for a low frequency current therapeutic device, or an electrode for extracting bioelectric information.

BACKGROUND ART

In known printed electrodes for biological use, the effective area of use of the electrode interface had been the rate-determining step in the output or input of the current. For example, when silver (Ag) is used as the anode printed electrode for iontophoresis and silver chloride (AgCl) is used as the cathode printed electrode, Ag is converted to AgCl on the anode surface when a current flows and, as a result, AgCl having a large electrical resistance covers the surface of the Ag and the effective surface of the Ag is reduced. Thus, the current falls along with time when a constant voltage of a direct current or pulse type is applied, i.e., a so-called deterioration phenomenon of the electrode occurs. In the case of electrodes for monitoring biological activity, this becomes a cause for occurrence of noise.

DISCLOSURE OF INVENTION

In view of the above-mentioned conditions of the prior art, the object of the present invention is to provide a printed electrode for biological use which suppresses the deterioration of the electrode by enlarging to the maximum extent, the number of electroconductive microgranules which can be used on the surface of the bioelectrode and which ensures the maintenance of a stable current over a long period of time.

In accordance with the present invention, there is provided a printed electrode for biological use comprising a support on which is printed an ink paste or binder containing hydrophilic microgranules comprising hydrophilic polymers or water-soluble substances and electroconductive microgranules.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be explained in detail below with reference to the drawings.

Figure 1 is an explanatory view illustrating an example of use of conventional iontophoresis electrode.

Figure 2(a) is an explanatory view of an iontophoresis porous electrode of the present invention.

Figure 2(b) is an explanatory view of another support for the electrode of Fig. 2(a).

Figure 3 is an explanatory view of a simplified device of the present invention.

Figure 4 illustrates the changes in the current showing a first embodiment of the present invention.

Figure 5 illustrates the changes in the current showing a second embodiment of the present invention.

Figure 6 illustrates the changes in the current showing a control example of the present invention.

BEST MODE FOR WORKING THE INVENTION

According to the present invention, there is provided a printed electrode for biological use comprised by impregnating, under mixing, in an ink paste and/or binder in an organic solvent having a relatively low boiling point one or more types of microgranules of a hydrophilic polymer or a water-soluble saccharide or salt or other water-soluble substance together with one or more type of electroconductive microgranules (silver, nickel, titanium, silver chloride, carbon, etc.) followed by printing this or directly sintering it on a support or heating it under reduced pressure or ordinary pressure to remove the organic solvent to thereby form a film or rod, whereby the effective area of the electrode surface is increased at the time of application of an aqueous solution or water-containing gel and the current stability is increased.

The features of the present invention will now be explained.

When producing the printed electrode for biological use according to the present invention, as the hydrophilic microgranules, at least one type of saccharide selected from glucose, fructose, mannitol, hydrolyzed starch, D-sorbitol, xanthane gum, etc.; at least one type of cellulose derivatives selected from carboxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, carboxymethylethylcellulose etc.; at least one type of hydrophilic polymer selected from polyvinylalcohols, etc.; at least one type of salts selected from sodium chloride, potassium chloride, calcium chloride, potassium phosphate, sodium dihydrogenphosphate, potassium dihydrogenphosphate, calcium dihydrogenphosphate, sodium hydrogenphosphate, potassium hydrogenphosphate, calcium hydrogenphosphate, sodium hydrogencarbonate, sodium acetate, calcium pantothenate, and sodium pantothenate, etc.; and at least one type of water-soluble vitamin selected from iron pyrophosphate, ascorbic acid, etc. are blended in an electroconductive ink paste. Further, the range of the size of the hydrophilic microgranules is not particularly limited but is preferably 3 to 200 μm, more preferably 3 to 50 μm.

Further, when producing the printed electrode according to the present invention, it is possible to use an electroconductive metal paste ink composition comprising, as an electroconductive ink paste, at least one type of binder selected from the group consisting of polyesters, polypropylene, polyethylene, polyethers, polyurethanes, methacrylic resins, epoxy resins, poly(vinyl chloride), poly(vinyl acetate), poly(vinylidene chloride) and copolymers of vinyl chloride with vinyl acetate or vinylidene chloride or acrylonitrile or ethylene, and copolymers of vinyl acetate with vinylidene chloride or

acrylonitrile or ethylene, in which is included 20 to 90% by weight, preferably 60 to 80% by weight, of at least one type of electroconductive microgranules (size of 0.1-100 μm) selected from the group consisting of silver, silver chloride, titanium, nickel, platinum, etc. containing 1 to 50% by weight, preferably 5 to 30% by weight, of the above-mentioned hydrophilic microgranules.

We will now explain one example of the case of use of the electrode structure of the invention as a silver chloride electrode for iontophoresis. In general, as shown in Fig. 1, the silver electrode (1) of the anode portion (1A) faces the biological surface through a drug solution holder (2) or hydrophilic gel (3), while the silver chloride electrode (4) of the cathode portion (2A) contacts the biological surface through the hydrophilic gel (5). The present invention, as shown by the example shown in Fig. 2(a), is an electrode having the structure of water soluble microgranules (6) uniformly dispersed in a silver print ink (7). When the iontophoresis is started, the microgranules are gradually dissolved in the water permeated from the gel or the aqueous solution. As a result, electrically, a porous electrode structure is formed. Accordingly, it becomes possible to ensure a stable current over a longer period of time, compared with a conventional silver or silver chloride printed electrode, wherein only the surface can be used. Figure 2(b) shows a modification of the shape of the electrode support (12) comprised of the same member or a combination of different members playing the role of the support shown in Fig. 2(a) and a connection means for electrical connection with the outside. (13) is the connection terminal for electrical contact with the outside.

Further, the electrode structure of the present invention is able to sufficiently meet its objectives of use after being stored in a dry state until just before use or being stored in a moist state in contact with a gel etc.

We will now explain an example of the method for manufacturing the electrode.

That is, one or more types of hydrophilic microgranules made of, for example, a hydrophilic polymer, water-soluble saccharide, or salt are mixed in and impregnated, together with one or more types of electroconductive microgranules (e.g., silver, nickel, titanium, silver chloride, carbon, etc.), with an ink paste or binder in an organic solvent having a relatively low boiling point and are printed or directly sintered on a support or heated under reduced pressure or ordinary pressure to remove the organic solvent to form a film shaped or rod shaped electrode.

Examples of the above-mentioned support are resins such as polyester, polyethylene, polypropylene, polyvinyl chloride, cellophane, nylon, polyimide, polyvinylidene chloride, polystyrene polycarbonate, etc. and nonwoven fabrics of such as cellulose, cellulose ester, nitrocellulose, rayon, polyester nylon etc. These are formed as a member having softness or hardness, but the material and shape are not particularly limited.

To further clarify the effects of the present invention, an explanation will be made of an experiment in a physiological saline solution using as an example a silver chloride electrode. The experiment was carried out using the simplified device shown in Fig. 3.

The electrodes, silver, and silver chloride, were set in parallel and a constant voltage of 3V was applied across the electrodes as the iontophoresis voltage. The stability of the current at that time was measured and evaluated.

EXAMPLES

The present invention will now be explained in further detail by examples and experiments using the electrodes, but the invention is by no means limited to the examples.

Example 1

The experiment was performed using a silver-sodium chloride electrode obtained by heating and curing a mixed ink paste comprised of 55 to 95% by weight (preferably 70% by weight) of a heat curing electroconductive silver paste "DW-250H-5" (made by Toyobo) and 5 to 45% by weight (preferably 30% by weight) of hydrolyzed starch (made by Wako Pure Chemical Industries) (average particle size is not more than 32 μm) at 150°C for 15 minutes. Across the anode Ag-starch and the cathode AgCl, depolarizing pulsatized iontophoresis was applied at a constant voltage of 3V, 40 kHz, and 30% duty. As shown in Fig. 4, a substantially stable current could be supplied even after 3 hours.

Example 2

The experiment was performed using a silver-sodium chloride-starch electrode obtained by heating and curing a mixed ink paste comprised of 55 to 95% by weight (preferably 70% by weight) of a heat curing electroconductive silver paste "DW-250H-5" (made by Toyobo), 22.5 to 2.5% by weight (preferably 15% by weight) of sodium chloride powder (average particle size is not more than 32 μm), and 22.5 to 2.5% by weight of hydrolyzed starch (made by Wako Pure Chemical Industries) (average particle size is not more than 32 μm) at 150°C for 15 minutes. Across the anode Ag-starch and the cathode AgCl, depolarizing pulsatized iontophoresis was applied at a constant voltage of 3V, 40 kHz, and 30% duty. As shown in Fig. 5, a substantially stable current could be supplied even after 3 hours.

Control Example

As a control, the experiment was conducted on just a heat cured electroconductive silver paste "DW-250H-5" (made by Toyobo), without the addition of sodium chloride, hydrolyzed starch, and other hydrophilic microgranules (additive free). The electrode curing conditions and the conduction conditions were made the same as with the above examples. As shown in Fig. 6, compared

with Example 1, in the case where no hydrophilic microgranules were added, the current clearly fell within 15 minutes from the start of the experiment.

INDUSTRIAL APPLICABILITY

As explained above, the present invention holds the water soluble microgranules or hydrophilic polymer microgranules between the electroconductive microgranules. When used as a bioelectrode, for example, when used for iontophoresis, moisture is taken up from the chlorine ion containing aqueous solution or gel by the water soluble microgranules or hydrophilic polymer microgranules and a porous electrode structure is formed during electrical conduction. As a result, it is possible to increase the effective interface surface area of the electroconductive microgranules and thereby to maintain a stable current for a long period.

Further, the present invention can be used for applications as bioelectrodes as represented by electrodes for low frequency therapeutic devices and electrodes for extracting bioelectric information in addition to the above-mentioned iontophoresis electrodes.

LIST OF REFERENCES IN DRAWINGS

1. Silver electrode
1A. Anode portion
2. Chemical holder
2A. Cathode portion
3. Hydrophilic gel
4. Silver chloride electrode
5. Hydrophilic gel
6. Hydrophilic microgranules
7. Silver paste
8. Silver paste electrode
9. Stirrer
10. Silver chloride electrode
11. Physiological saline solution
12. Electrode support
13. Connection terminal for electrical contact

Claims

1. A printed electrode for biological use comprising a support on which is printed an ink paste or binder containing a hydrophilic microgranules comprising hydrophilic polymers or water-soluble substances and electroconductive microgranules.

2. A printed electrode as claimed in claim 1, wherein said hydrophilic microgranules are at least one type selected from saccharides, cellulose derivatives, salts, and water-soluble vitamins.

3. A printed electrode as claimed in claim 2, wherein the particle size of the hydrophilic microgranules is 3 to 200 μm.

4. A printed electrode as claimed in claim 1, wherein said electroconductive microgranules are at least one type selected from carbon, silver, silver chloride, titanium, nickel, and platinum.

5. A printed electrode as claimed in claim 4, wherein the particle size of the electroconductive microgranules is 0.1 to 100 μm.

6. A printed electrode as claimed in claim 1, wherein said binder is at least one type selected from polyester, polypropylene, polyethylene, polyether, polyurethane, methacrylic resin, epoxy resin, poly(vinyl chloride), poly(vinyl acetate), vinyl chloride copolymer, vinyl acetate copolymer, ethylene copolymer, and vinylidene chloride copolymer.

Fig.1
PRIOR ART

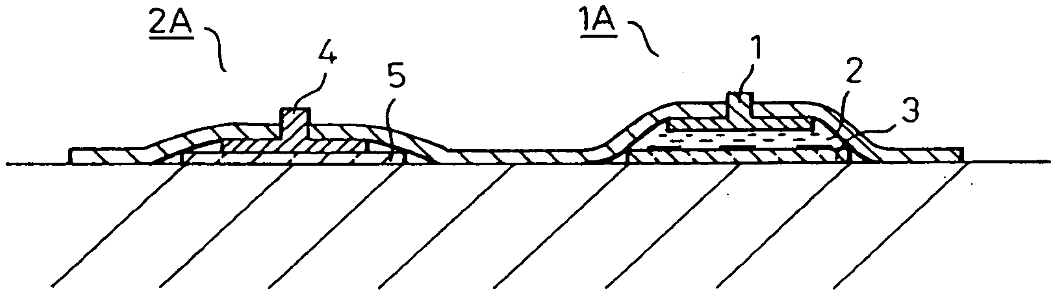


Fig.2(a)

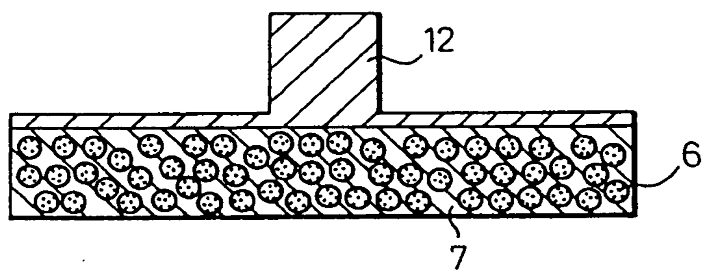


Fig.2(b)

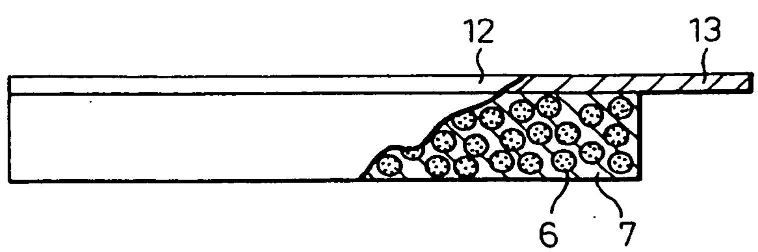


Fig.3

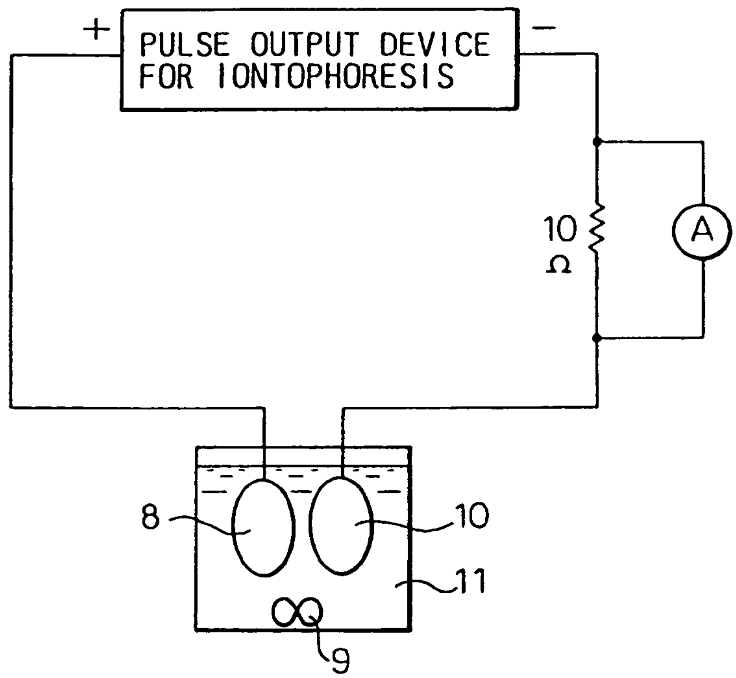
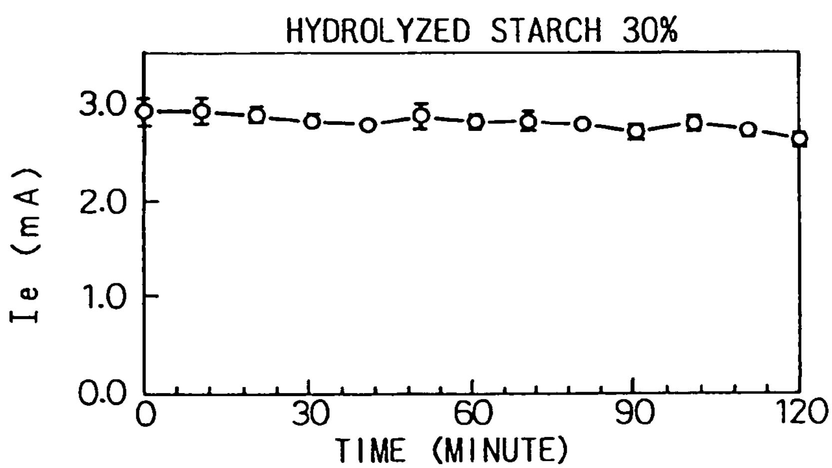

+
PULSE OUTPUT DEVICE
FOR IONTOPHORESIS
−
10
Ω
A
8
10
11
9

Fig.4


HYDROLYZED STARCH 30%
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3.0
2.0
1.0
0.0
0
30
60
90
120
TIME (MINUTE)

Fig.5

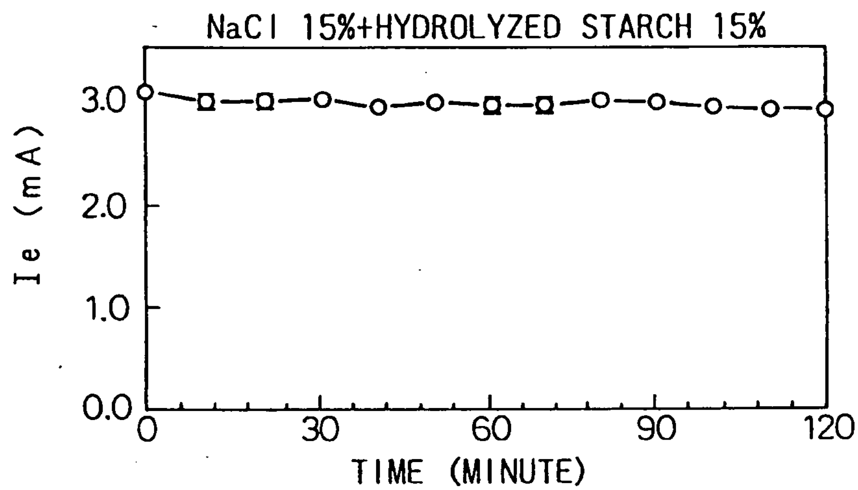
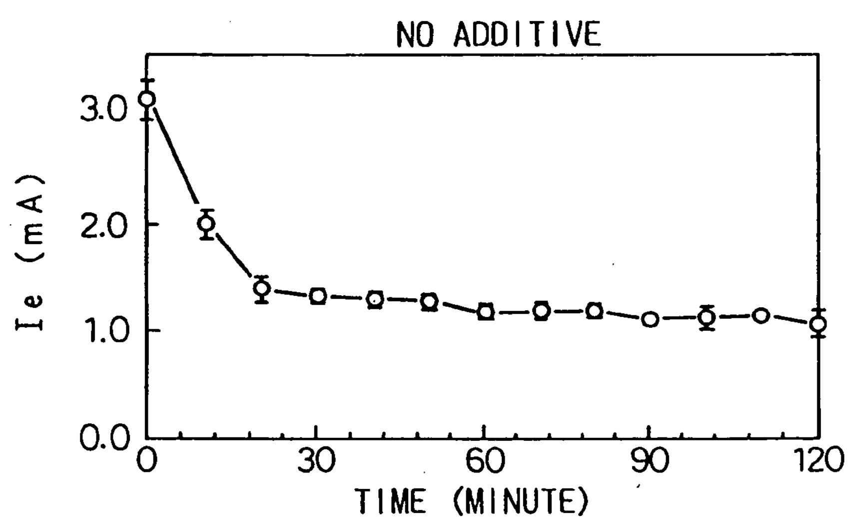

NaCl 15%+HYDROLYZED STARCH 15%
Ie (mA)
3.0
2.0
1.0
0.0
0
30
60
90
120
TIME (MINUTE)

Fig.6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Ie (mA)
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2.0
1.0
0.0
0
30
60
90
120
TIME (MINUTE)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP95/00203

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl^6 A61N1/04, A61B5/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl^6 A61N1/04, A61B5/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1945 - 1994
Kokai Jitsuyo Shinan Koho 1971 - 1994

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, A, 58-149734 (Fujikura Kasei K.K., Nippon Koden Kogyo K.K.), September 6, 1983 (06. 09. 83) (Family: none)	1 - 6

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
April 14, 1995 (14. 04. 95)	May 2, 1995 (02. 05. 95)

Name and mailing address of the ISA/	Authorized officer
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